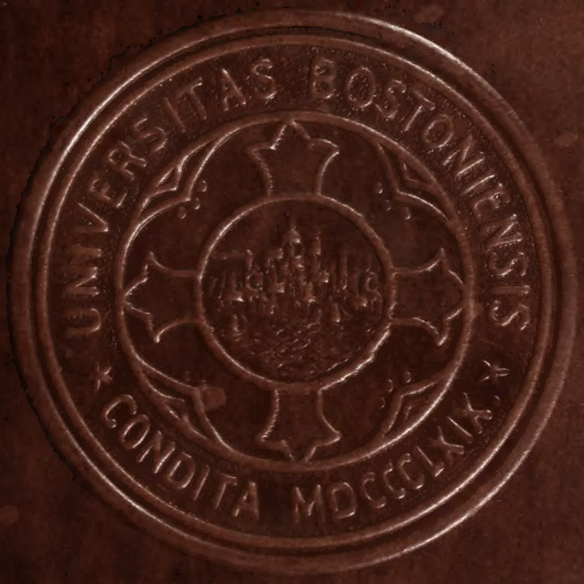

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Cupp, Samuel B.

BOSTON UNIVERSITY

GRADUATE SCHOOL

Thesis

CAUSES OF BEARING CORROSION

by

Samuel Beck Cupp

(B.S., Dickinson College, 1939)

submitted in partial fulfillment of the

requirements for the degree of

Master of Arts

1941

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by

First Reader Edward O. Holmes, Jr.
Professor of Chemistry

Second Reader Chester M. Alter
Asst. Professor of Chemistry

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Introduction

The purpose of this investigation is to determine what substance or substances in oil are responsible for the corrosion of cadmium alloy bearings.

Modern development in the construction of internal combustion engines has included the introduction of certain bearing alloys, such as cadmium-nickel and cadmium-silver, which are much more susceptible to corrosion than the more conventional babbit bearings. If these new bearings had been used in engines twenty-five years ago, because of engine construction they probably would not have been any more corroded than babbit bearings. At that time engines were operated almost entirely on the all loss method. The oil was added to the crankcase, passed over the bearings not more than a few times, and was burned up. In modern engines, the same oil passes over the bearings again and again. Oxidation and decomposition products are formed and accumulated in the oil. Some of these are corrosive and some are inert, but I have been unable to find any such classification of them.

C. H. Bierbaum[1] suggests several possible causes of corrosion. It may be a purely chemical reaction; it may be an electrolytic effect, due to either the difference of electrical potential between metals or an electrical current induced or direct; or lastly, it may be electrolysis accompanied by a chemical reaction. In his investigations, he took into consideration

(1) Bierbaum, C. H., Iron Age, No. 9: 20-21, 58 (1933)

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(1) Bierbaum, G. E., Iron Age, No. 9: 80-81, 96 (1920)

only the purely chemical effect. Oils with or without additions, such as oleic acid or sulfur, were put into a beaker and placed on a laboratory hot-plate at a temperature of 150° F. Air was introduced through a glass tube and was bubbled continuously through the oil. Various polished metalographic specimens of different bearings were placed one at a time in the oils. The resulting effects were given microscopical study. He found that the pure fatty acids are all more or less corrosive upon the ordinary metals and that subjecting them to oxidation increases the corrosive effect. He does not point out any acid as being particularly harmful. He even concludes that the addition of oleic acid has a twofold beneficial effect. It not only increases the capillary affinity for the metal surfaces but causes a slight etching effect on the softer crystals which increases the amount of oil in the film. He found stearic acid to be rather passive, but found that it shows slight chemical activity after oxidation. Sulfur was found to be one of the most corrosive constituents that he added to the lubricating oils.

In fear of trouble from corrosion, some people have been led to watch the neutralization or acid value of used oil. G. A. Round[2] thinks that in both ideas they are misled because the type of acid is more important than the amount. This point is shown by the results of engine corrosion tests.[2] There was no correlation between the observed corrosion or weight loss of bearings and the acid numbers for the oils used in his tests.

(2) Round, G. A., S. A. E. Journal 43, 301-341 (1938)

One oil with a low neutralization number caused bad bearing corrosion while another oil having a fairly high acid number was not found to be exceptionally corrosive.

M. R. Fenske[3] estimated the composition of the volatile acids formed on oxidation of lubricating oils by means of the Ducleaux procedure. A mixture of formic, acetic, propionic, and butyric acids in a molecular proportion of 3 to 5 to 0.7 to 1 gave a curve which followed well that for the unknown acid mixture obtained from the oxidized oils. He also found considerable non-volatile acids but did not estimate their composition. He found very little variation in the relative amounts of the different volatile acids obtained from the oxidation of various oils. He stated that the proportion of formic acid was probably higher than indicated, and probably constituted 40 to 50 percent of the total volatile acids. Although these values may not be the same for the oils oxidized by use in an engine, they do at least give an idea of their probable values.

A possible factor which may contribute to corrosion is the electrode potential of metals and alloys in contact with oils and the resulting electromotive force of the various connected parts. Hovorka and Anthony[4] found that an actual measurable electromotive force exists and measured it for several metals and alloys. A cell composed of aluminum-oil-cadmium silver gave an electromotive force of about 0.2 volts at 170° C.

(3) Fenske, M. R., Ind. & Eng. Chem., Analytical Edition, 13: 51-60 (January 15, 1940)
(4) Hovorka, F. and Anthony, J. K., Ind. & Eng. Chem., 29: 959-962 (1937)

A steel-oil-cadmium silver cell gave an electromotive force of about 0.5 volts at the same temperature. Usually an appreciable voltage did not appear until a temperature of about 100° C. was reached. With a cadmium silver-oil cadmium silver annealed cell, the results were very irregular with frequent changes in polarity. The conductivity of the oils is an important factor since the amount of chemical reaction caused by a difference in potential is proportional to the amperage. Hovorka and Anthony did not attempt to measure the difference in potential between points on the surface of the same bearing. Each metallic part has a definite potential against its surrounding, which ordinarily is oil. This potential may be large or may be so small that it is immeasurable. However, whichever it may be, the final result is the presence of a large number of cells each contributing its electromotive force. This may cause various chemical reactions which may prove to be destructive in their action on the surfaces of the various metallic parts. For example, let us take a crankshaft that is composed of a metal "y" and a bearing made of a metal or alloy "x." These two are contacted by some oil and the whole setup acts as a galvanic cell. The following results may be expected as the cell works: x or y may dissolve because of its electrolytic solution pressure; x or y may serve as electrodes at which some of the components of the oil are oxidized and then the oxidation products may chemically attack the metals in contact with it; the oxidation products may cause further chemical reactions in the oil

which may result in corrosive substances. Thus it may be possible that the electrode potential is either directly or indirectly responsible for some corrosion.

Waivrzinick[5] investigated sixty-eight lubricating oils and greases for electrical resistance, acid numbers, tension between electrodes, and intensity of current. He found that a high internal resistance is accompanied by a low acid number. He points out that corrosion of motor parts may be due to galvanic currents generated between different metal parts, the oil serving as the electrolyte.

Although the identity of a definite constituent of oxidized oil which causes bearing corrosion has not yet been established, some attempts have been made to decrease corrosion by the addition of so-called inhibitors. An oil which has incorporated with it a small proportion of a free aliphatic amine base, such as triethanolamine, and a small amount of an organic nitro reducing compound such as nitrophenol is found to be practically non-corrosive.[6] Another organic compound which when present in lubricating oil to the extent of from 0.05 to 0.5 percent substantially retards corrosion is a dialkyl polysulfide having the formula RSS_nSR, where n is one or two.[7] 0.1 percent of an inhibitor formed by the reaction of sulfur with a diaryl amine such as diphenylamine or phenolthiazine may be used.(8)

(5) Waivrziniok, Z., Automobiltechn, 35: 428-430 (1932)
(6) U. S. Patent 2,189,788
(7) U. S. Patent 2,192,874
(8) U. S. Patent 2,190,648

Triphenyl arsine (suitable in a proportion of about 0.2 percent) is used to inhibit the tendency of oils to corrode bearings of metals such as cadmium-silver, cadmium-nickel, and copper-lead alloys.[9] p-Ethoxy phenylmorpholine[10], ethyl cyanide[11], cyanoacetamide[12], methylene amine acetonitrile[13], toluenediamine[14], and benzanilide[15] are other corrosion inhibitors. Corrosion that is due to acid-forming oils can be prevented in a cadmium or lead containing bearing by the addition of indium.[16] It may be applied by electrodeposition, with or without subsequent diffusion into the bearing metal by subjection to heat, or it may be alloyed with the metal.

(9) U. S. Patent 2,139,726
(10) U. S. Patent 2,139,726
(11) U. S. Patent 2,139,086
(12) U. S. Patent 2,139,087
(13) U. S. Patent 2,139,088
(14) U. S. Patent 2,187,353
(15) U. S. Patent 2,139,758
(16) British Patent 504,953

Experimental

A small amount of a single substance known to exist in oxidized oil or a substance which might be found in used crankcase oil was added to a sample of commercial lubricating oil (Havoline 50). The sample of oil was placed in a tube made by sealing one end of a 6-inch piece of 8 mm. Pyrex tubing. Pieces of cadmium-nickel or cadmium-silver bearings approximately 5 mm. in width were placed in the sample. The tubes were sealed and kept at a temperature of 170° C. for 100 hours. Then they were opened and examined to determine the extent of corrosion caused by the particular contaminant added to the oil.

No attempt was made to purify any of the chemicals used. The formic acid and formaldehyde contained 10 and 63 percent water, respectively. All the other substances were almost 100 percent pure although only the acetic acid was a C. P. reagent.

The manufacturer's specifications for the cadmium alloy bearings which were used were as follows:

	Cadmium Silver Bearing	Cadmium Nickel Bearing
Copper	.15 to .25%	.05% max.
Tin	.10% max.	.01% max.
Lead	.05% max.	.02% max.
Silver	1.75 - 2.25%	none
Nickel	none	1.00 - 1.50%
Cadmium	Remainder	Remainder

The first two runs were made in a constant temperature bath using glycerine covered with a layer of mineral oil and paraffin as the liquid medium. The mineral oil reduced very greatly the fumes of acrolein resulting from a slight decomposition of the glycerine. However, the stirring necessary for

circulation and uniform temperature mixed the glycerine with the oil layer and caused considerable fumes to escape. During the second run, the fumes were partially eliminated by drawing them off continuously with a water pump. This still was not considered satisfactory, so an air bath was used for the rest of the runs. The air bath kept the temperature constant enough for our purpose, $170^{\circ} \pm 5^{\circ}C$.

A satisfactory method for the quantitative determination of the small amount of corrosion with which we are dealing could not be found. Since the bearings were only a thin layer of cadmium-nickel alloy fastened to a steel base, we could not use the loss of weight method for analysis. Even if we had used solid alloy bearings, it is doubtful whether the slight amount of corrosion would have been detectable by a loss of weight. The oil from one of the most corroded samples was ashed, but a measurable amount of cadmium or silver was not obtained. Therefore this method was discarded. Bierbaum[2] examined his samples microscopically and did not report any quantitative results. Since we could not find a satisfactory method of analysis, we attempted to devise one.

The corroded surface of the bearing is rough and dark. Usually the more corroded it is, the deeper will be the pits and the darker the color. This causes it to absorb or scatter most of the light which strikes it. On the contrary, an uncorroded bearing has a smooth shiny surface which reflects most of the incident beams at an angle equal to the angle of incidence. Only a small amount of light is scattered. This is the

basis of our proposed method of measuring corrosion. The amount of reflected light is measured by means of a photoelectric cell and a very sensitive galvanometer.

Two different light sources were tried. The one found most convenient and satisfactory was an ordinary 25 watt electric light. Monochromatic light from a sodium lamp was the other source tried. The results vary somewhat. The main trouble with the sodium lamp was the lack of intensity. The lamp must be placed so close to the sample that all of the non-parallel beams of light cannot be eliminated before striking the sample to be analyzed. Since the voltage of the commercial 110 volt source was not absolutely constant, a slight variation of several percent was noticed in the galvanometer readings.

Since it was desirable to have only parallel rays of light strike the bearing sample, it was necessary to eliminate the other rays. This was done by means of an aluminum tube lined with a layer of black cotton velvet. The end of the tube where the light emerges was partially closed by an aluminum plate with a rectangular hole just slightly larger than the bearing sample cut into it. This eliminated excess light and also some non-parallel beams not absorbed by the cotton velvet.

The support for the bearing was made from a strip of zinc. Its width is diminished at the upper end so that none of it is exposed to the beam of light. There are several catches on the side so that the bearing may be always placed in the same position. This is verified by duplicate readings of the galvan-

ometer when the same sample is removed and replaced.

The angle between the incident beam and the reflected beam is about 90°. The angle of incidence is therefore 45°. With one set of samples the angle was varied and slightly different results were obtained. Table 1 shows the effect of changing the angle. When the angle of incidence is increased the relative galvanometer readings for the most corroded samples are also increased. A decrease in the angle of incidence caused a decrease in the galvanometer readings for the same samples. Variations of the angle of incidence for the samples which were only slightly corroded did not cause much change in the readings. An angle of incidence of 45° was found to be most convenient for the apparatus used and is considered to be satisfactory. A considerable decrease in the angle causes an increased possibility of the light from the source directly reaching the photoelectric cell and thus giving erroneous readings. Mechanical difficulties prevent the use of a large angle of incidence.

The photoelectric cell is a cetron C-E 2 obtained from the Continental Electric Company. It has a sensitivity of approximately 120 microamperes per lumen. It is steady and has proved very satisfactory. It is protected from all extraneous light by a cardboard can with a rectangular hole cut in it to admit only the desired beams of light.

The current for the photoelectric cell is supplied by two 45 volt "B" batteries connected in series. Very little

Table 1

The Effect of a Change of the Angle of Incidence

Angle of Incidence	60°		45°		30°	
Sample Number	Galvanometer Readings					
	End A	End B	End A	End B	End A	End B
J - 7	.45	.50	.40	.40	.30	.30
J - 8	.60	.65	.50	.55	.40	.40
J - 9	.50	.60	.40	.45	.40	.40
J - 10	.60	.95	.45	.90	.45	.95
J - 11	4.0	5.4	4.2	4.9	3.8	4.6
J - 12	3.9	4.9	4.0	5.5	3.9	4.6
J - 13	5.9	6.3	6.0	6.2	5.4	5.8

Table I

The Effect of a Change of the Angle of Incidence

Angle of Incidence	60°		45°		30°	
	Galvanometer Readings					
Couple Number	Rod A	Rod B	Rod A	Rod B	Rod A	Rod B
1 - 7	.25	.50	.40	.40	.30	.30
7 - 8	.30	.85	.30	.35	.40	.40
7 - 9	.30	.60	.40	.45	.40	.40
7 - 10	.30	.95	.45	.30	.45	.35
7 - 11	4.0	5.4	4.2	4.0	3.0	4.8
7 - 12	3.2	4.9	4.0	3.8	3.9	4.6
7 - 13	8.3	6.3	6.0	8.2	6.4	6.8

current is drawn off from them so that the voltage does not change appreciably. A galvanometer with a sensitivity of .005 millimicroamperes was used to measure the current that flowed through the photoelectric cell.

In tables 4 to 9 are given the galvanometer readings for various samples. A highly polished bearing sample 5 mm. in width was taken as a standard. The light was adjusted so that it gave a galvanometer reading of 10.0 before readings for the other samples were taken. The width of some samples varied slightly. A correction of the galvanometer readings was made to compensate for this change in surface area. The first readings in the column marked "before polishing" were made on the samples after they were washed thoroughly with benzene. The next column contains the readings made after the samples were rubbed briskly with a clean cloth. This probably removed any film left by the benzene and in some cases a residue left by the oil. The next column contains the readings that were obtained when a sodium lamp was substituted as a source of light. In tables 4 to 6, the samples were not polished any more than they had been for the previous column or readings. Since they had been standing for a week between the two sets of readings, they were slightly tarnished. This accounts for the readings in general being lower for the sodium light than for the polished sample with ordinary light. The samples recorded in table 7 were polished again before they were measured with sodium light. The results show that polishing slightly before a measurement

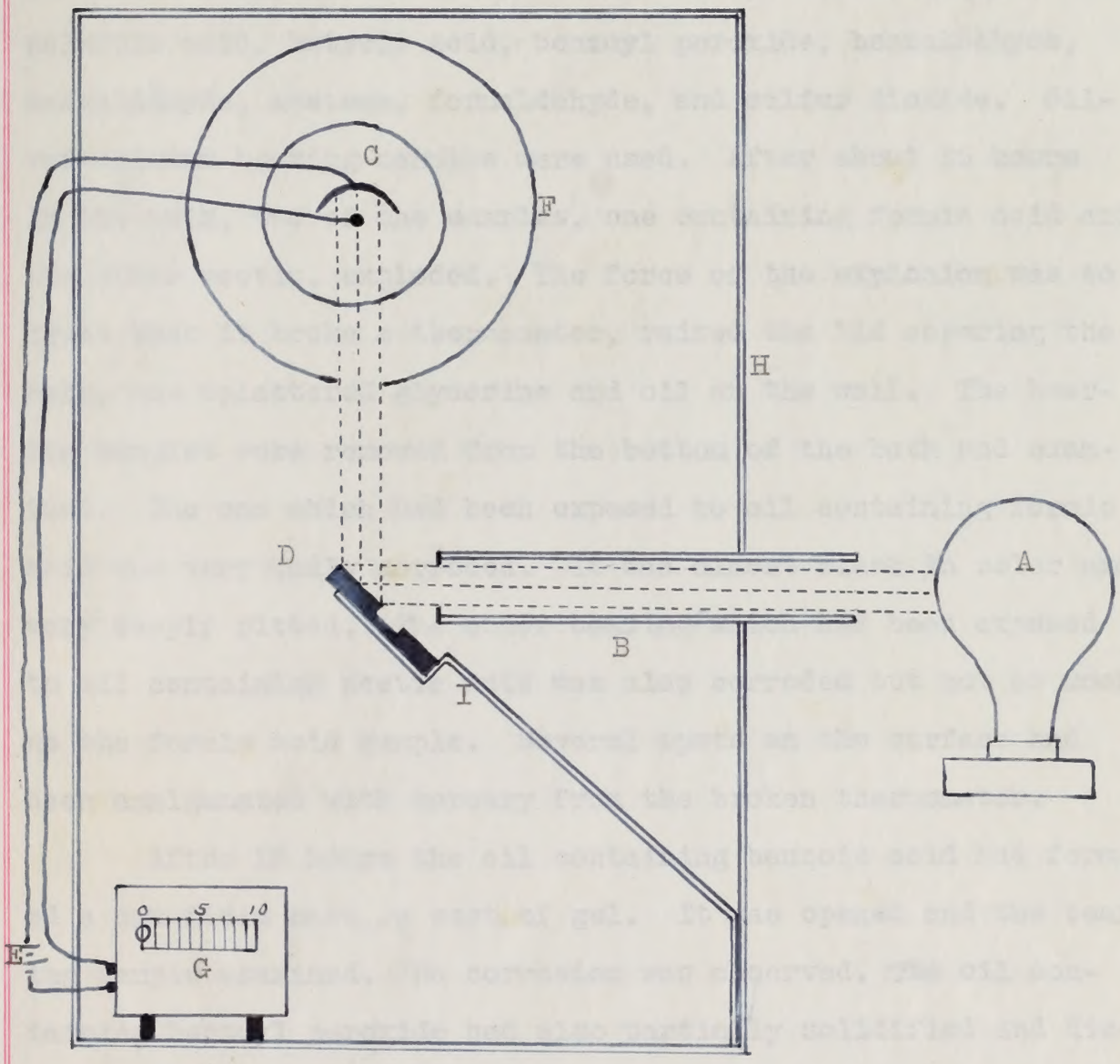
raises the reading considerably. Not very much of a difference is noted between ordinary electric light and monochromatic sodium light as the source of light when the samples were examined in an identical condition. Table 2 shows a comparison of readings when ordinary and polarized light were used as sources of light. There was no detectable difference observed between the reflectivity when ordinary electric light was used and when the same light was polarized by passing it through a sheet of polaroid.

The reflectivity method for measuring corrosion has many flaws. Any variation in the size of the sample before exposure causes appreciable errors. However, corrections for this are easily made. Any discoloration or change in reflectivity causes abnormally low readings. The manner of washing the sample free from the oil and deposits from contaminated oil has a definite effect on the reading. Rubbing the surface of the sample with a cloth changes the reading greatly. Exposure of a polished sample to air even for a short time reduces the reading. Any deposits such as lacquers on the sample are falsely interpreted by this method as corrosion. However, the method still has some practical value. It detects corrosion which is not visible. It gives a good indication of the amount of corrosion, even if not an absolute measurement of it. Two samples which give identical readings can be considered, with little error, to be corroded the same amount. However, the method does not give a linear relationship between corrosion and galvanometric reading.

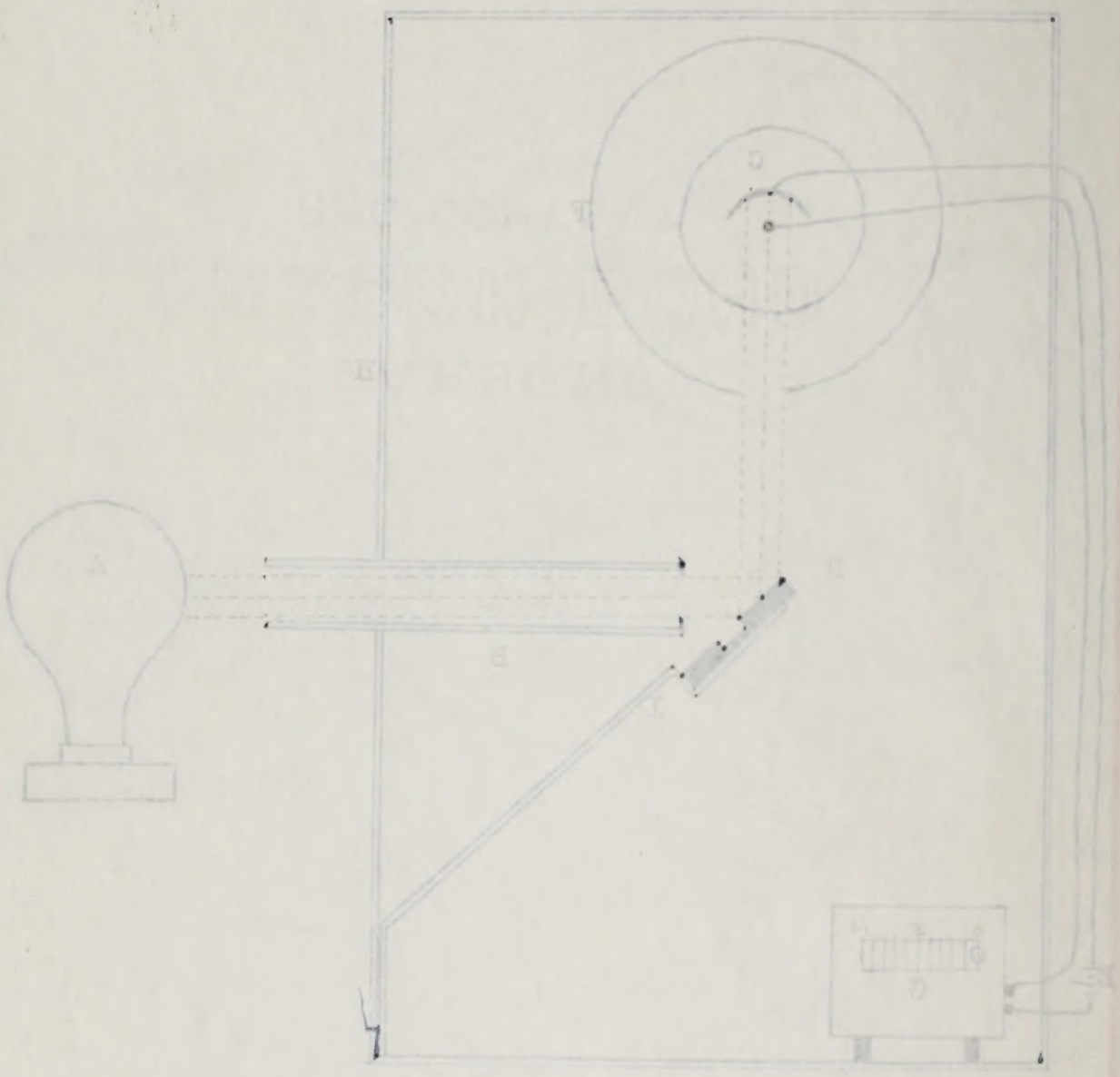
Table 2

Sample Number	Galvanometer Reading: Polarized Electric Light	Galvanometer Reading: Ordinary Electric Light
K - 1	1.4	1.4
K - 2	1.6	1.6
K - 3	1.7	1.7
K - 4	2.7	2.7
K - 5	2.7	2.8
K - 6	4.0	4.0

Fig. I



A- Light source
B- Tube lined with Cotton Velvet
C- Photoelectric Cell C-E2
D- Bearing Sample
E- 90 Volts- Two 45 volt batteries
F- Cardboard Can
G- Galvanometer
H- Wall
I- Support for Bearing



The first run was made using oils to which had been added formic acid, acetic acid, benzoic acid, stearic acid, palmitic acid, butyric acid, benzoyl peroxide, benzaldehyde, acetaldehyde, acetone, formaldehyde, and sulfur dioxide. Silver-cadmium bearing samples were used. After about 15 hours in the bath, two of the samples, one containing formic acid and the other acetic, exploded. The force of the explosion was so great that it broke a thermometer, raised the lid covering the bath, and splattered glycerine and oil on the wall. The bearing samples were removed from the bottom of the bath and examined. The one which had been exposed to oil containing formic acid was very badly corroded. It was almost black in color and very deeply pitted. The other bearing which had been exposed to oil containing acetic acid was also corroded but not as much as the formic acid sample. Several spots on the surface had been amalgamated with mercury from the broken thermometer.

After 15 hours the oil containing benzoic acid had formed a non-fluid mass, a sort of gel. It was opened and the bearing sample examined. No corrosion was observed. The oil containing benzoyl peroxide had also partially solidified and discolored. The bearing sample was not corroded except in several spots where probably the solid benzoyl peroxide had come in contact with the surface. A benzene solution of the oil was deep red in color.

New samples containing formic acid, acetic acid, benzoic acid, and benzoyl peroxide were put in the bath to replace those

removed. Since benzoyl peroxide was not appreciably soluble in cold oil, it was heated with oil and shaken to mix thoroughly before being sealed in the tube with the bearing sample. It still did not dissolve but formed a fine suspension.

After 100 hours in the bath at 170° C. all the samples were opened. The results are listed in table 3. Formic acid (A-1) caused by far the most corrosion. The formaldehyde (A-12) also caused bad corrosion. Benzoyl peroxide (A-7) attacked the surface but did not cause deep pitting. Acetic acid (A-2) caused some corrosion but not as much as was expected. Butyric acid (A-6) caused a slight amount of corrosion. The higher fatty acids caused only a slight amount of corrosion. All the other substances caused little corrosion if any.

Table 4 shows the effect of various other substances on cadmium-nickel bearing samples. The galvanometer reading may be taken as an indication of the amount of corrosion. Two used oils to which nothing was added ((C-1), (C-2)) discolored the bearing samples but caused only very slight corrosion. Metal salts were added to several samples. Copper sulphate when added to a used oil and permitted to come in contact with the bearing surface caused bad corrosion (C-6). When copper sulfate crystals in new oil were kept from coming in contact with the bearing, no corrosion occurred (D-11). Ferric chloride ((C-7), (D-12)) caused considerable corrosion even when direct contact with the bearing was prevented with asbestos. Iron powder (C-8) when in direct contact did not cause even the

Table 3

Number of Silver-Cadmium Bearing Sample	Substance Added	Weight of Substance Added, grams	Percent Added	Corrosion Observed
A - 1	Formic Acid	.15	5	Very bad.
A - 2	Acetic Acid	.15	5	Apprec. amount.
A - 6	Butyric Acid	.15	5	Slight.
A - 3	Benzoic Acid	.15	5	Very slight.
A - 4	Stearic Acid	.15	5	Very slight.
A - 5	Palmitic Acid	.15	5	Very slight.
A - 7	Benzoyl Peroxide	.15	5	Bad.
A - 8	Benzaldehyde	.15	5	Very slight.
A - 9	Acetaldehyde	.15	5	Very slight.
A - 10	Acetone	.60	20	Very slight.
A - 11	Sulfur Dioxide	-	Saturated	Very slight.
A - 12	Formaldehyde	.5/ 37%	6	Very bad.

Table 4

Cd-Ni Bearing Sample Number	Oil	Subst. added to 3 grams of oil sample	Galvanometer Reading Ordinary Electric Light Polish. End A	Polish. End B	Unpol. End A	Unpol. End B	Sodium Light - End A	Sodium Light - End B	Corrosion Observed
C-1	Used B-1	Nothing	1.8	2.0	2.2	2.5	1.8	2.0	Discol. Slightly Cor.
C-4	Used B-7	Nothing	1.2	1.2	1.7	1.8	1.3	1.4	Discol. Slightly Cor.
C-6	Used B-1	.5 grams $CuSO_4$ Cryst.	0.4	0.4	0.5	0.6	0.4	0.5	Very badly corroded.
C-7	Used B-1	.5 grams $FeCl_3$ powder	0.4	1.2	0.5	1.6	0.4	1.1	Badly cor.
C-8	New	.5 grams Fe powder	2.4	4.9	4.5	5.7	4.1	5.4	None
D-11	New	.5 grams $CuSO_4$ Cryst. Asbestos Protection	1.9	2.1	3.0	3.6	2.4	2.5	None
D-12	New	.5 grams $FeCl_3$ with Asbestos Protection	0.8	0.9	2.0	2.1	1.2	1.2	Consid.
E-1	New	Benzoyl Peroxide: Saturated	2.1	2.1	4.0	5.2	3.7	4.9	None
E-2	New	Nothing	2.2	2.5	6.1	6.2	5.5	5.6	None
F-1	New	.5 grams Sulfur	2.0	2.7	3.2	3.7	2.6	3.3	Discol. Slightly Cor.
H-6	New	.2 grams $PbAc_2$	0.6	0.7	1.1	1.9	0.6	1.1	Badly cor.
H-7	New	.2 grams Phenol	1.5	1.7	2.2	2.7	1.5	2.0	None
H-10	New	.1 grams Salicylic Acid	0.6	0.7	2.6	3.5	2.5	3.5	Very slightly

slightest amount of corrosion. Previously, solid benzoyl peroxide was shaken and heated to form a fine suspension in the oil. This time solid benzoyl peroxide was let stand in the oil for several days at room temperature. The oil was then decanted from the solid. It caused no corrosion, probably because none of it dissolved in the oil. Sulfur (F-1) caused a bad discoloration but very little corrosion. Lead acetate (H-6) caused bad corrosion. Phenol (H-7) had no effect on the bearing sample. Salicylic acid (I-10) caused a very slight amount of corrosion.

Table 5 shows the effect of oil containing different concentrations of formic acid. As the letters of the sample numbers indicate, it is a combination of samples from the different runs. From the data, it seems as if the amount of corrosion is dependent upon the total amount of formic acid in the oil. Almost any concentration causes some amount of corrosion, but in the samples of very low concentration the total amount of acid present is not enough to cause a visible amount.

Table 6 again shows the effect of formic acid. The galvanometer readings give a good indication of the extent of corrosion. The lower the concentration of acid, the higher the reading is. There are several exceptions. For some unknown reason, several large spots comprising almost half the surface of G-3 was not corroded at all. Other spots were badly corroded. This is the reason for the galvanometer reading being larger than for the next sample G-4 where corrosion is not nearly as

Table 5

Cd-Ni Bearing Sample Number	Grams of formic acid in 3 grams oil	Percent Acid	Galvanometer Reading Ordinary Electric Light Unpol. End A	Unpol. End B	Polish. End A	Polish. End B	Sodium Light - End A	Sodium Light - End B	Corrosion Observed
C-3	.025	0.8	1.0	1.2	2.5	2.7	1.8	2.0	Not bad.
C-2	.012	0.4	1.1	1.2	1.2	1.4	1.2	1.4	More.
C-5	.006	0.2	0.8	1.0	1.5	1.9	1.4	1.8	Slight.
C-9	.003	0.1	1.1	1.2	1.6	1.6	1.4	1.5	Slight.
D-8	.0015	0.05	2.2	2.7	3.1	3.8	2.7	3.2	Very slight.
D-9	.0008	0.025	1.8	1.9	2.7	2.7	2.5	2.6	Slight.
D-10	.0004	0.012	2.6	2.8	3.9	4.8	3.7	4.7	Very slight.
F-2	.0004	0.012	2.5	2.9	3.7	4.4	3.4	3.7	Very slight.
F-3	.0002	0.006	1.9	2.7	3.2	4.5	2.9	4.0	Very slight.
F-4	.0001	0.003	2.1	2.2	3.1	4.0	2.5	4.0	Very slight.
F-5	.00005	0.0015	2.8	2.9	4.8	5.5	4.0	5.1	None.
F-6	.000025	0.0008	3.7	3.8	5.7	6.5	5.0	5.3	None.
F-7	.000012	0.0004	2.2	3.2	4.6	6.2	4.0	5.0	None.
F-8	.000006	0.0002	2.5	3.2	5.7	6.1	4.0	4.5	None.

Table 5

24-Hr. Sample Number	Grams of Formic acid in 3 grams oil	Percent Acid	Galvanometer Reading Ordinary Zinc-Sodium Couple.					Color Reaction Observed
			Trip. A	Trip. B	Iodine Ind. A	Iodine Ind. B	Starch Ind.	
C-1	.025	0.8	1.0	1.2	2.5	2.7	1.0	Not bad.
C-2	.012	0.4	1.1	1.2	1.2	1.4	1.2	More.
C-3	.006	0.2	0.8	1.0	1.2	1.0	1.4	Slight.
C-4	.003	0.1	1.1	1.2	1.2	1.0	1.4	Slight.
D-5	.0015	0.05	2.8	2.7	3.1	2.8	2.7	Very slight.
D-6	.0008	0.025	1.8	1.8	2.7	2.5	2.8	Slight.
D-10	.0004	0.012	2.6	2.8	2.8	3.2	4.7	Very slight.
E-2	.0004	0.012	2.3	2.3	3.7	4.4	3.7	Very slight.
E-3	.0002	0.006	1.9	2.7	3.2	3.9	4.0	Very slight.
E-4	.0001	0.002	2.1	2.2	3.1	4.0	3.0	Very slight.
E-5	.00005	0.0015	2.8	2.9	4.0	4.0	3.1	None.
E-6	.000025	0.0008	3.7	3.0	3.7	4.8	3.0	More.
E-7	.000013	0.0004	3.8	3.2	4.2	4.9	3.0	None.
E-8	.000006	0.0002	3.6	3.2	3.7	4.1	4.0	None.

Table 6

Cd-Ni Bearing Sample Number	Grams of formic acid in 3 grams oil	Percent Acid	Galvanometer Reading Ordinary Electric Light Unpol. End A	Unpol. End B	Polish. End A	Polish. End B	Sodium Light - End A	Sodium Light - End B	Corrosion Observed
G-1	0.043	1.4	0.5	0.6	0.6	0.6	0.3	0.35	Very bad.
G-2	0.022	0.7	1.0	1.0	1.2	1.4	.80	.80	Bad.
G-3	0.011	0.35	1.8	2.3	3.3	4.4	2.5	2.6	Consid.
G-4	0.005	0.18	1.2	1.2	2.8	3.1	2.5	2.5	Slight.
G-5	0.0025	0.09	1.7	3.3	2.2	4.7	2.2	4.1	Slight.
G-6	0.0012	0.045	1.1	2.2	3.1	5.0	2.6	4.3	Slight.
G-7	0.0006	0.022	4.0	5.3	7.4	8.8	5.7	7.5	Slight.
G-8	0.0003	0.011	3.2	4.0	6.3	7.0	4.7	5.4	Very slight.
G-9	0.00015	0.006	3.4	4.0	6.3	8.4	4.5	6.2	Very slight.
G-10	0.00008	0.003	3.1	4.2	6.7	8.8	5.0	6.4	None.
G-11	0.00004	0.0015	3.0	4.1	7.0	9.0	5.8	7.3	None.
G-12	0.00002	0.0008	4.0	5.2	8.3	9.1	7.0	8.9	None.
G-13	0.00001	0.0004	3.0	3.6	5.6	7.3	4.5	5.8	Very slight.
G-14	0.000005	0.0002	3.2	3.9	5.5	8.6	4.7	6.4	None.

Table 6

Sample Number	Grams of Formic acid in 5 grams oil	Percent Acid	Chlyrmonomer Reading Ordinary Alco- Sodium Turpol. Pollab. A B A B	Corrosion Observed
C-1	0.065	1.4	0.6 0.6 0.6 0.6 0.6 0.6	Very bad.
C-2	0.032	0.7	1.0 1.0 1.2 1.4 .80 .80	Bad.
C-3	0.013	0.30	1.0 2.2 3.2 4.4 2.2 3.8	Doubtful.
C-4	0.005	0.12	1.2 1.2 2.8 3.1 2.2 2.2	Slight.
C-5	0.0025	0.05	1.4 2.2 2.2 4.2 2.2 2.1	Slight.
C-6	0.0012	0.025	1.1 2.2 3.1 3.0 2.2 2.2	Slight.
C-7	0.0006	0.012	4.0 5.2 7.4 8.8 6.2 7.6	Slight.
C-8	0.0003	0.011	3.2 4.0 6.2 7.0 4.2 5.4	Very slight.
C-9	0.00012	0.006	3.4 4.0 6.2 6.4 4.2 6.2	Very slight.
C-10	0.00006	0.003	3.1 4.2 6.2 6.0 3.0 6.4	None.
C-11	0.00004	0.0015	3.0 4.1 7.0 8.0 5.8 7.2	None.
C-12	0.00002	0.0008	4.0 5.2 6.2 8.1 7.0 8.0	None.
C-13	0.00001	0.0004	3.0 8.6 6.6 7.2 4.2 6.6	Very slight.
C-14	0.000005	0.0002	3.2 5.0 8.2 8.6 4.7 8.4	None.

bad but is uniform.

Since it was thought that the irregularity of results in table 6 might be due to lack of circulation of the oil around the bearing sample while the run is being made, another run was made (table 7). However, during this run the samples were occasionally inverted to insure at least some mixing. Much care was taken to see that the size of the bearing samples and their reflectivity before exposure was uniform. Graph 2 shows the regularity of the increase in the galvanometer readings with the logarithm of dilution. It is a fairly smooth curve compared to the curve in Graph 1. Graph 1 is rather irregular. This is probably due to improper mixing while the sample is being exposed to the oil and slight variations in the reflectivity of the samples before exposure.

Since the bearing sample, because of construction, is separated into two parts, two readings are given for each sample. As the data shows, the two portions are often not corroded to the same extent. The difference is especially noted when very little corrosion has taken place. In the graphs, the average galvanometer readings are plotted. Curve I in graph 2 shows almost a linear relationship between the galvanometer reading and the logarithm of the dilution of formic acid with oil.

Table 8 shows the effect of the different concentrations of acetic acid, propionic acid, and formaldehyde. Acetic acid, even when quite concentrated in the oil, does not cause very

Table 7

Cd-Ni Bearing Sample Number	Grams of formic acid in 3 grams oil	Percent Acid	Galvanometer Reading Ordinary Electric Light Unpol. End A	Unpol. End B	Polish. End A	Polish. End B	Sodium Light - End A	Sodium Light - End B	Corrosion Observed
I-1	0.075	2.5	.30	.30	.30	.30	.30	.30	Very bad.
I-2	0.038	1.25	.40	.45	.40	.40	.35	.35	Very bad.
I-3	0.019	0.6	.65	.70	.90	1.0	.80	.90	Bad.
I-4	0.010	0.3	.70	.75	1.1	2.1*	.90	1.7*	Bad in spots.
I-5	0.005	0.15	.70	.75	1.1	1.3	1.2	1.3	Consid.
I-6	0.0025	0.08	1.1	1.3	1.9	2.1	1.7	2.1	Slight.
I-7	0.0012	0.04	1.2	1.4	2.5	2.7	2.5	2.7	Slight.
I-8	0.0003	0.01	1.4	1.8	3.3	3.4	3.8	4.4	Slight.
I-9	0.00015	0.005	2.0	2.1	4.5	5.0	5.0	5.5	Very slight.

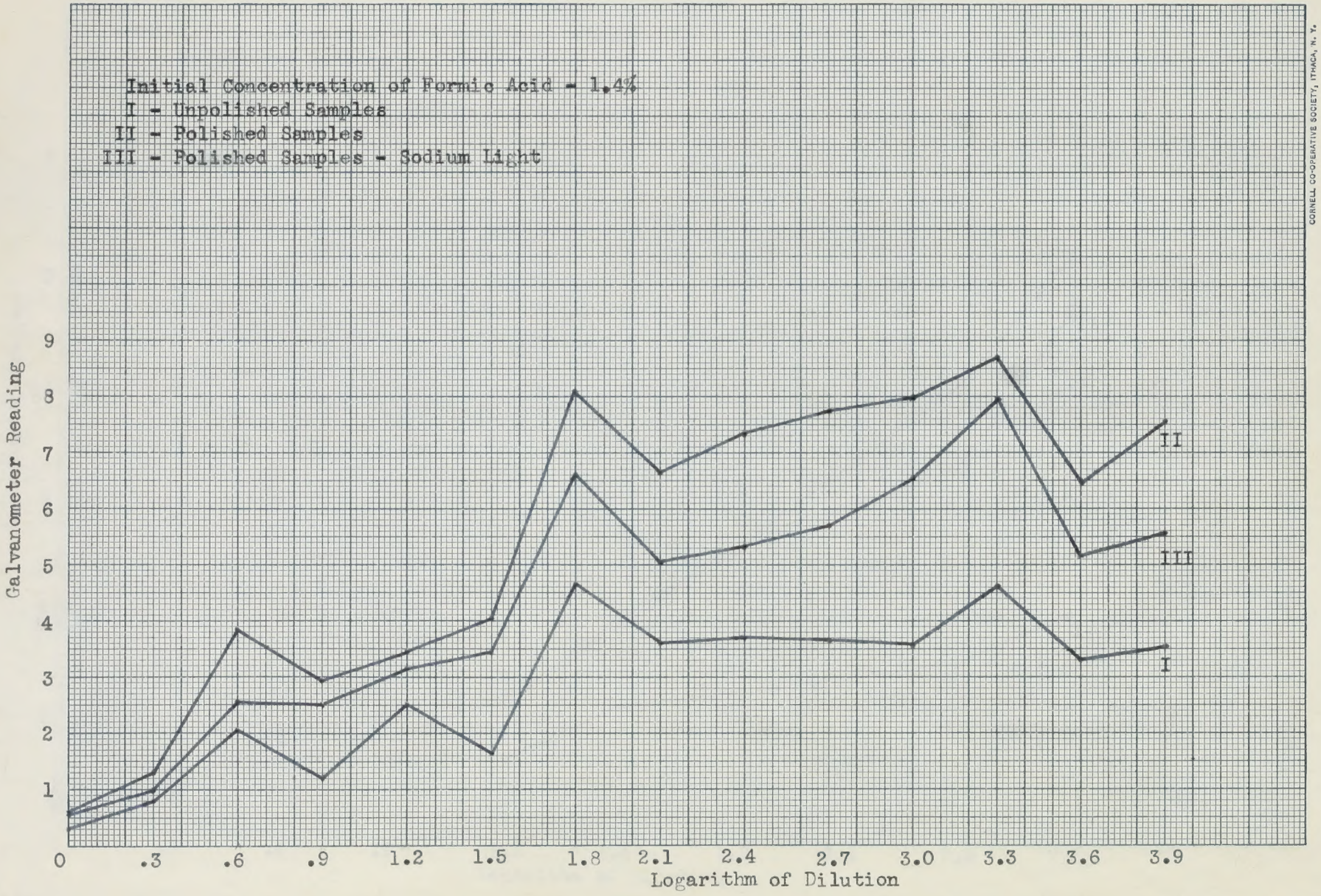
* Irregularity

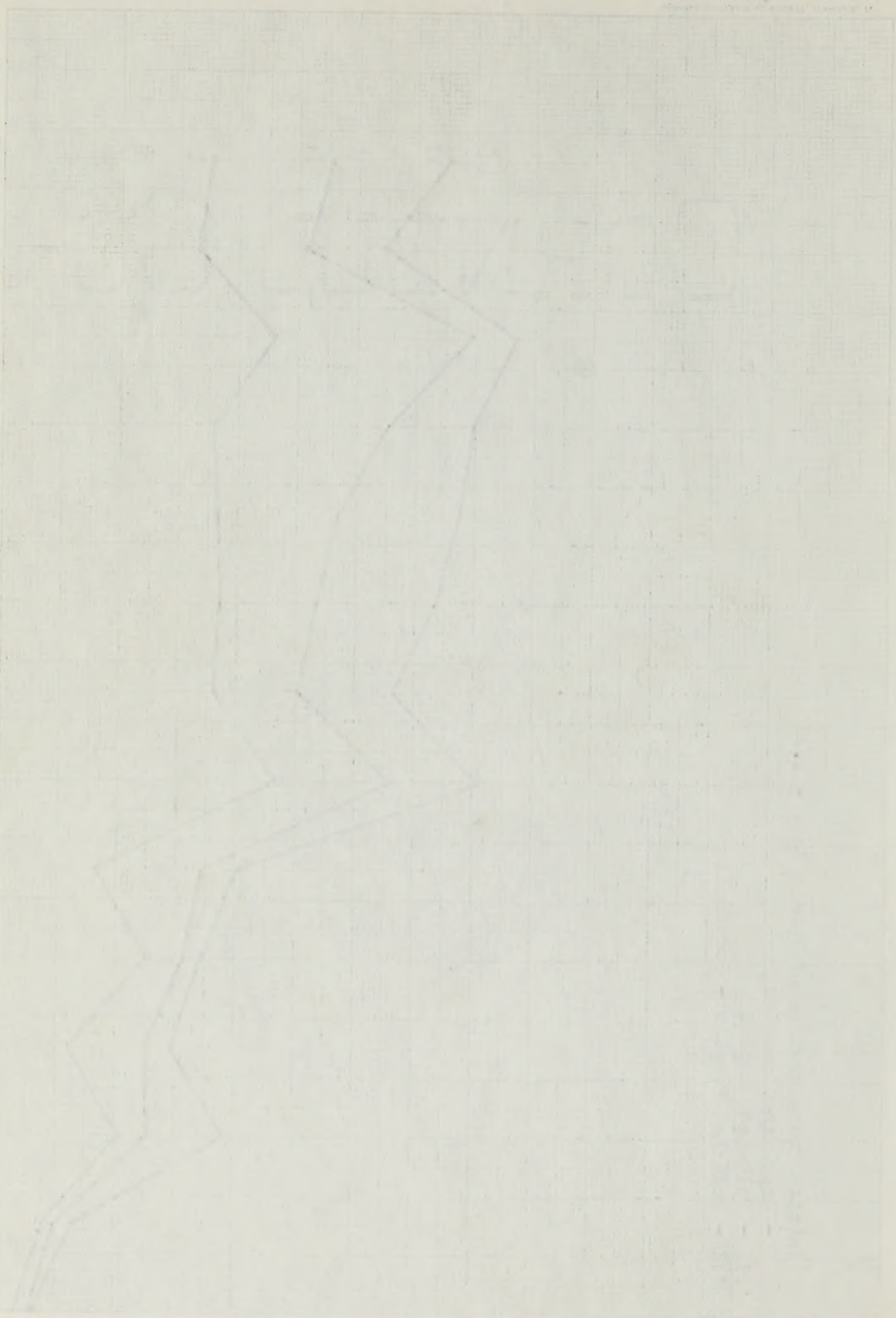
Table 7

Cd-Ni Bearing Sample Number	Grease of Formic acid in 3 grease oil	Percent Acid	Calvanometer Reading Orthotary Elec- Reduction trie Light Unpol. Polar. End End End End A B A B	Corrosion Observed
I-1	0.095	2.5	.80 .30 .30 .80 .30 .30	Very bad.
I-2	0.080	1.25	.60 .65 .60 .60 .55 .55	Very bad.
I-3	0.010	0.6	.05 .70 .80 1.0 .00 .30	Bad.
I-4	0.010	0.3	.70 .75 1.1 2.1 .00 1.7*	Bad in spots.
I-5	0.006	0.15	.70 .75 1.1 1.5 1.5 1.5	Consid.
I-6	0.0025	0.08	1.1 1.5 1.9 2.1 1.7 2.1	Slight.
I-7	0.0012	0.04	1.2 1.4 2.5 2.7 2.5 2.7	Slight.
I-8	0.0003	0.01	1.4 1.8 2.2 3.4 3.5 4.4	Slight.
I-9	0.00016	0.005	2.0 2.1 4.5 3.0 5.0 7.0	Very slight.

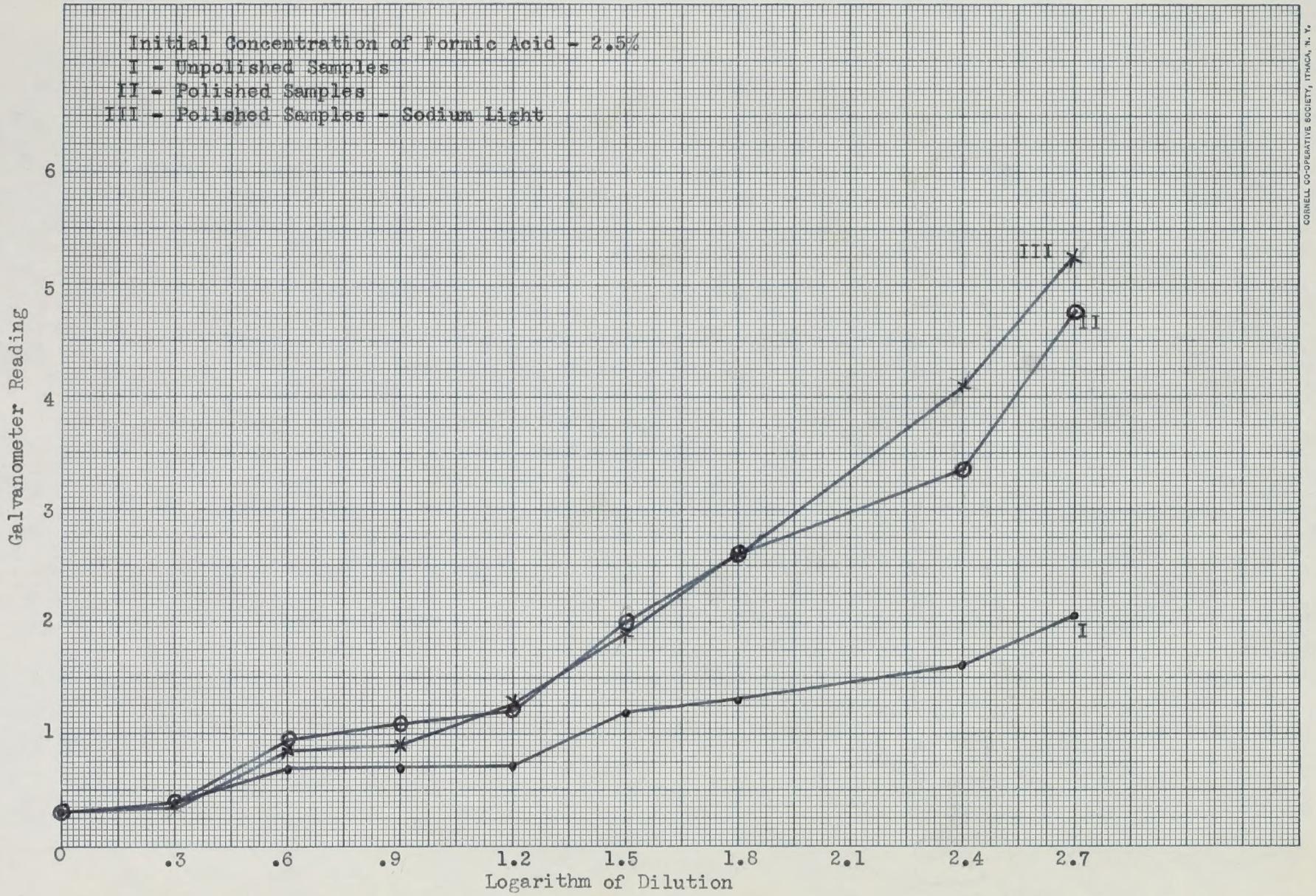
* Irregularity

Graph I


Initial Concentration of Formic Acid - 1.4%
I - Unpolished Samples
II - Polished Samples
III - Polished Samples - Sodium Light
Galvanometer Reading
9
8
7
6
5
4
3
2
1
0
.3
.6
.9
1.2
1.5
1.8
2.1
2.4
2.7
3.0
3.3
3.6
3.9
Logarithm of Dilution
II
III
I
CORNELL CO-OPERATIVE SOCIETY, ITHACA, N. Y.



Graph II


Initial Concentration of Formic Acid - 2.5%
I - Unpolished Samples
II - Polished Samples
III - Polished Samples - Sodium Light
Galvanometer Reading
0
1
2
3
4
5
6
.3
.6
.9
1.2
1.5
1.8
2.1
2.4
2.7
Logarithm of Dilution
III
II
I
CORNELL CO-OPERATIVE SOCIETY, ITHACA, N. Y.

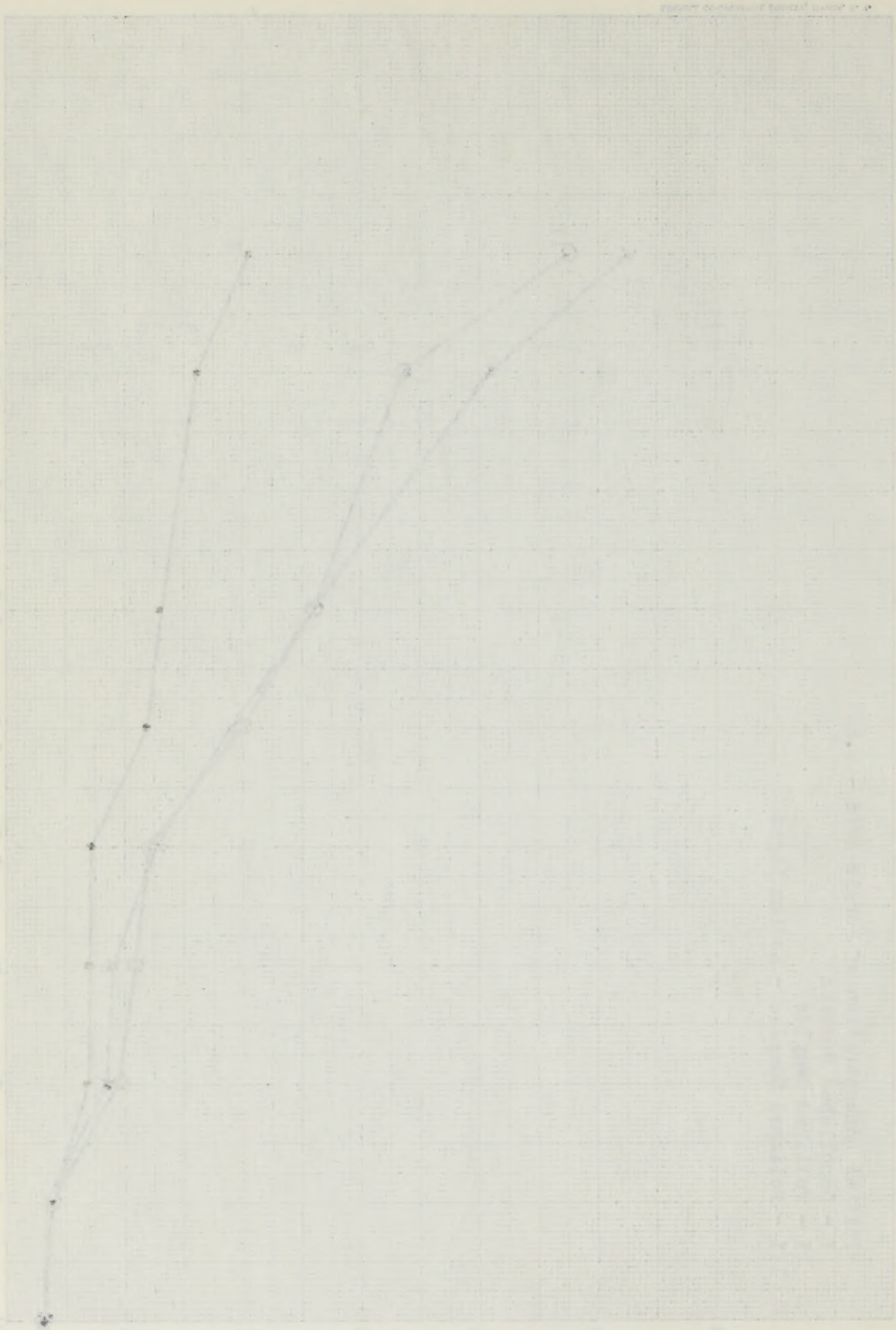


Table 8

Cd-Ni Bearing Sample Number	Grams of subst. in 3 grams oil	% Compos.	Galvanometer Reading Ordinary Electric Light Unpol. End A	Unpol. End B	Polish. End A	Polish. End B	Sodium Light - End A	Sodium Light - End B	Corrosion Observed
H-1	Acetic acid 0.04	1.3	1.5	1.9	2.2	4.6	1.8	2.6	Not badly corroded.
H-2	Acetic acid 0.02	0.65	2.4	2.9	3.6	5.0	2.4	3.5	Slight.
H-3	Acetic acid 0.01	0.32	2.0	2.2	3.2	3.3	2.1	2.1	Slight.
H-4	Acetic acid 0.005	0.16	1.4	1.6	2.8	5.0	2.0	3.3	Slight.
H-5	Acetic acid 0.0025	0.08	1.4	1.9	2.9	5.2	1.9	3.7	Slight.
H-8	Propionic acid 0.07	2.4	0.8	2.0	2.2	4.7	1.2	2.4	Slight.
H-9	Propionic acid 0.035	1.2	1.3	1.3	2.2	3.3	1.7	1.7	Slight.
H-10	Propionic acid 0.018	0.6	1.5	1.8	2.6	2.8	1.9	2.1	Slight.
H-11	Propionic acid 0.009	0.3	1.5	1.5	2.2	2.5	1.7	2.0	Slight.
F-9	Formaldehyde 0.055	1.8	0.4	0.5	.40	.50	.35	.40	Corroded and caked.
F-10	Formaldehyde 0.028	0.9	0.6	0.8	.60	.90	.60	.70	Corroded and caked.
D-2	Formaldehyde 0.0092	0.3	1.6	2.0	2.1	2.6	2.2	2.2	Not bad.
D-3	Formaldehyde 0.0046	0.15	1.8	2.0	3.0	3.0	2.6	2.7	Slight.
D-4	Formaldehyde 0.0023	0.08	2.0	2.2	3.6	4.1	3.2	4.0	Very slight.
D-5	Formaldehyde 0.0012	0.04	1.2	1.7	2.0	2.6	2.0	2.6	Slight.

bad corrosion. 0.15 percent formic acid caused more corrosion than did 1.3 percent acetic acid. From this we might conclude that formic acid is over nine times as corrosive as acetic acid. Lower concentrations of acetic acid caused only slight corrosion. Propionic acid caused even less corrosion than acetic acid. Formaldehyde caused considerable corrosion. It also polymerized and decomposed on the bearing surface, forming an irregular cake of lacquer in the two most concentrated samples. Its action is probably due to its oxidation to formic acid. It takes a fairly high concentration to cause considerable corrosion.

Table 9 shows the effect of concentrated sulfuric acid on cadmium nickel bearing samples. The four samples J-7, J-8, J-9, J-10, containing the greatest amount of acid, were very badly corroded. The other samples J-11, J-12, J-13, J-14, containing a smaller amount of acid, were attacked only very slightly. When the acid was added to the oil the oil turned black almost immediately. This undoubtedly decreased the acid concentration. In the samples J-11 to J-14 this probably accounts for the fact that corrosion was very slight. Almost all of the acid was used in decomposing the unstable oil and consequently very little was left which could attack the bearing. After having been washed with benzene the corroded bearing surface was yellow in color. Some of this corroded material was scraped off and analyzed. It dissolved readily in dilute hydrochloric acid and evolved considerable hydrogen sulfide.

Table 9

Cd-Ni Bearing Sample Number	Wgt. of H_2SO_4 in 3 grams sample	% H_2SO_4	Galvanometer Reading Ordinary Electric Light Unpol. End A	Unpol. End B	Polish. End A	Polish. End B	Sodium Light Unpol. End A	Unpol. End B	Polish. End A	Polish. End B	Corrosion Observed
J-7	.185	6.2	.35	.35	.40	.40	.30	.32	.35	.40	Very bad.
J-8	.092	3.1	.30	.34	.50	.55	.27	.30	.40	.50	Very bad.
J-9	.046	1.6	.30	.33	.40	.45	.29	.29	.40	.40	Very bad.
J-10	.023	.8	.30	.33	.45	.90	.25	.29	.40	.75	Very bad.
J-11	.012	.4	1.4	1.7	4.2	4.9	1.3	1.6	3.7	4.6	Slight.
J-12	.006	.2	1.6	2.4	4.0	5.5	1.6	2.2	4.0	5.1	Very slight.
J-13	.003	.1	1.9	2.3	6.0	6.2	1.8	2.2	5.4	6.2	Very slight.
J-14	.0015	.05	1.9	2.4	7.5	8.6	1.8	2.3	7.1	8.2	Practically none.

(38)

The solution was neutralized and hydrogen sulfide was passed into it. A bright canary yellow precipitate formed. Therefore the corrosion product was almost entirely cadmium sulfide.

Table 10 shows a comparison of the concentrations of formic acid, acetic acid, propionic acid, sulfuric acid and formaldehyde which give about the same galvanometer readings. At the concentrations indicated they can be considered as being almost equally corrosive.

An Attempt to Measure Potential Differences

An attempt was made to determine if a difference in potential exists between different points on the surface of a cadmium-silver bearing. When points were touched with copper wires, a slight deflection of a very sensitive galvanometer resulted. However, results were not reproduceable and the polarity as well as magnitude varied for the same points. An attempt to improve the results was made by using a liquid junction of 10 percent and, later, a saturated potassium chloride solution. This again failed to give constant results. Silver chloride electrodes were next tried, using a saturated silver chloride solution as the liquid junction. Since the resistance was very high, a potential amplifier was used. This also failed. When a trace of potassium chloride was added, still no constant readings were obtained.

Table 10

Comparison of the Concentration of Various Substances Which Cause Similar Corrosion

Cadmium Nickel Bearing Sample Number	Grams of Substance in 3 gram oil	% Composition	Galvanometer Reading
I-6A	.0025 Formic Acid	.08	1.9
D-2A	.009 Formaldehyde	.3	2.1
J-10A)* J-11A)	.017 Sulfuric Acid	.6	2.3
H-1A	.04 Acetic Acid	1.3	2.2
H-8A	.07 Propionic Acid	2.4	2.2

* Average value for two samples given.

Table IO

Comparison of the Concentration of Various
Substances Which Cause Similar Corrosion

Cadmium Nickel Bearing Sample Number	Grams of Substance in 5 gram oil	% Composition	Calvanometer Reading
I-6A	.008 Formic Acid	.08	1.9
D-2A	.009 Formaldehyde	.9	2.1
I-10A)* I-11A)	.017 Sulfuric Acid	.6	2.3
H-1A	.04 Acetic Acid	1.3	2.3
H-2A	.07 Propionic Acid	2.4	2.3

* Average value for two samples given.

Conclusion

Formic acid, even when present in oil in small amounts, causes corrosion. It is far more corrosive than any of the other organic acids investigated. As the molecular weight of the acids increases, their corrosiveness decreases. Palmitic acid and stearic acid even when present in rather large quantities cause only very slight corrosion. Formaldehyde causes fairly bad corrosion. This is probably due to its oxidation to formic acid. Benzoyl peroxide causes some corrosion and it is possible that sludges containing peroxides contribute to corrosion. Sulfuric acid caused bad corrosion.

From the results of this investigation, it is rather easy to see that as shown by G. A. Round[2] the neutralization number of an oil may not necessarily be an indication of its corrosiveness. The neutralization number of a used oil indicates the amount of acid in the oil. This acid may consist almost entirely of the almost non-corrosive higher fatty acids such as stearic and palmitic acid or it may contain a considerable amount of very corrosive formic acid and other low molecular weight corrosive acids. While an engine is in operation, the temperature of the oil is sufficient for most of the lower acids to be volatilized and thus escape. Therefore most of the formic acid formed probably either corrodes the bearings and other metal parts and is used up or volatilizes and is lost. The latter most likely predominates although enough of the former occurs sometimes to cause considerable trouble.

Some of the formic acid is probably oxidized directly to carbon dioxide and water. The higher fatty acids will accumulate in the oil and give a high acid number but will not cause much corrosion. The author thinks that a used oil is more corrosive than a new oil not because it contains an accumulation of oxidation materials but because it is less stable and is therefore more easily oxidized to non-accumulating corrosive substances.

Metal salts, if present in sufficient quantities, will cause some corrosion. However, they are usually present in very small amounts and are considered to be the result of wear and corrosion rather than the cause of it.

The reflectivity method of measuring bearing corrosion which was devised and applied in this work was found useful in comparison of the corrosiveness of purposely contaminated oils. It consists of the measurement of the relative amount of light reflected from a bearing sample by means of a photoelectric cell and a very sensitive galvanometer. The most convenient and satisfactory source of light was found to be ordinary electric light. A change in the angle of incidence of the light source was found to have only a slight effect on the relative reflectivity of corroded samples.

Abstract

An investigation to determine the cause of cadmium alloy bearing corrosion was made. The procedure employed was to add substances to a non-corrosive oil and determine their effect on a bearing sample when it was subjected to a temperature of 170°C. for 100 hours. The amount of corrosion was measured by the amount of light reflected from the sample. Both ordinary electric light and monochromatic sodium light were used. The amount of light reflected was measured by a photoelectric cell. The data recorded consists of galvanometer readings of the relative amount of current flowing through the cell.

It was found that the lower molecular weight organic acids cause corrosion. Formic acid caused much worse corrosion than an equivalent amount of any other acid. The higher fatty acids were only slightly corrosive. Formaldehyde was very corrosive, probably because of its oxidation to formic acid. Benzoyl peroxide caused considerable corrosion when present as a solid in suspension in the oil. Sulfuric acid caused bad corrosion. Benzoic acid, salicylic acid, phenol, acetaldehyde, acetone, and benzaldehyde did not cause any appreciable amount of corrosion.

An explanation is given as to why the neutralization number of an oil is not an absolute measure of its corrosiveness even though evidence is shown that acids cause corrosion.

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